Title of the Invention:

Ferritic Steel Sheet Concurrently Improved in Formability,
High-temperature Strength, High-temperature Oxidation Resistance, and
Low-temperature Toughness

BACKGROUND OF THE INVENTION

Field of the Invention:

This invention relates to a ferritic steel sheet concurrently improved in formability such as deep drawability, stretch formability and the like, high-temperature strength, high-temperature oxidation resistance, and low-temperature toughness, particularly a steel sheet that, being usable in a 800 – 900 °C high-temperature atmosphere, is suitable for utilization in automobile engine exhaust gas passage components.

Background Art:

Since ferritic stainless steels have a smaller thermal expansion coefficient than austenitic stainless steels and are excellent in thermal fatigue property and high-temperature oxidation property, they are used as heat-resistant materials in applications where thermal strain is an issue. Typical applications include automobile engine exhaust gas passage components such as exhaust manifolds, front pipes, catalyst carrier outer cylinders, center pipes, mufflers and tailpipes.

A trend seen in recent automobile engines is to increase exhaust gas temperature in order to improve exhaust gas purification efficiency and output. This has increased the need for high heat resistance (high-temperature strength and high-temperature oxidation resistance) particularly in the exhaust manifold, front pipe, outer cylinder of the catalyst carrier and other components near the engine. A tendency for the shape of exhaust gas passage components to become more complicated has also recently emerged. This is especially notable in the exhaust manifold and outer cylinder of the catalyst carrier, which are being formed in complex configurations by various methods, including

mechanical pressing, servo pressing, spinning and hydroforming. It is therefore not sufficient for the materials used in these components to be good merely in stretching elongation and bendability. They are now also required to be excellent in formability such as typically deep drawability and stretch formability, and the in-plane anisotropy of their workability has to be small. In addition, owing to the fact that consideration needs to be given to prevention of ductile fructuer and brittle cracking during secondary and tertiary machining, they must also be excellent in low-temperature toughness. Moreover, heat resistance cannot be sacrificed in the interest of improving formability and low-temperature toughness, because greater shape complexity increases the likelihood of thermal fatigue fracture occurring owing to concentration of thermal strain at a single location during engine starting and stopping and also boosts vulnerability to abnormal oxidation caused by the material temperature rising locally.

SUH409L and SUS430J1L are known as ferritic stainless steels having high heat resistance. SUH409L is commonly used as an exhaust gas passage component material because of its good workability and low-temperature toughness. However, the level of its heat resistance makes it unsuitable for applications in which the material temperature exceeds 800 °C. It is also lacks sufficient deep drawability for application to components with complicated shapes. SUS430J1L has excellent heat resistance that makes it usable at 900 °C. But it is hard and poor in formability.

In light of the foregoing, the following heat-resistant ferritic steels have been developed.

Patent Reference 1 among the references listed below teaches a ferritic heat-resistant stainless steel with a Cr level of 17.0 – 25.0%. This steel is added with Mo and Cu in combination to improve high-temperature strength and with Mn to suppress scale spalling. Degradation of impact value by Mo is overcome to some degree by combined addition of Cu and Ni. However, the steel's formability is not adequate to cope with the needs of complexly shaped exhaust gas passage components. And its high Cr content makes it disadvantageous from the cost aspect.

Patent Reference 2 teaches a 13% Cr ferritic stainless steel that exhibits heat resistance at least as good as an 18% Cr ferritic stainless steel and also has improved high-temperature salt corrosion property. In this steel, high-temperature strength is increased by ensuring the presence of solid solution Nb, high-temperature oxidation property is improved by liberal addition of Mn and Si, and NaCl-induced hat corrosion resistance is improved by the Si. As no particular consideration is given to improvement of formability and low-temperature toughness, however, the steel cannot adequately respond to the recent harsh requirements mentioned earlier.

Patent Reference 3 teaches a Nb-containing heat-resistant ferritic stainless steel with a Cr level of 11.0 – 15.5% that is aimed at improving high-temperature oxidation resistance and scale adherence. These properties are markedly improved by strictly constraining Mn/Sn within the range of 0.7 – 1.5. This Patent Reference also teaches improvement of low-temperature toughness and workability by Cu addition. Regarding workability, for example, it presents data showing that no cracking occurred in a 180-degree bending test. In light of the fact that demands regarding the shape of exhaust gas passage components are becoming more and more challenging, however, the materials used in these components have come to require excellent formability that is compatible with various forming methods (discussed later). Regarding this point, the steel of Patent Reference 3 pays no attention to deep drawability and other drawability-related stretch formability and, as such, cannot be considered capable of responding to today's severe requirements. In addition, its Cr content of 11.0% or greater is on the level required in a stainless steel, which is inconsistent with the desire to reduce cost by lowering the Cr content in exhaust gas passage components that do not necessarily require use of stainless steels.

Patent Reference 4 teaches a ferritic stainless steel for exhaust manifolds that contains Cr at 11 – 14%. This is a steel enhanced in high-temperature strength by positive addition of Si to a Nb-containing steel. Its high temperature can be considered to be the same as the steel of Patent Reference 3. As it does not give consideration to improving formability and low-temperature toughness beyond the

level of the prior art, however, it is incapable of thoroughly responding to the harsh demands placed on steels in recent years. It also needs further reduction in Cr level.

Patent Reference 5 teaches a ferritic heat-resistant steel for engine exhaust gas passage components having a Cr content of 8.0 – 10.0%. This is a steel that achieves better heat resistance than SUH409L while also reducing cost through low Cr content. This reference further teaches that Cu is effective for improving both low-temperature toughness and workability. Regarding workability, it was for example found to possess ductility on a par with SUH409L in tensile tests at room temperature. As it is not aimed at improvement of the in-plane anisotropy of ductility or deep drawability, however, it leaves unresolved the problem of imparting formability thoroughly matched to the needs of various forming methods (discussed later). Nor does it offer a method for consistently imparting excellent low-temperature toughness. Patent Reference 5 can therefore not be viewed as sufficiently responding to the recent severe requirements with respect to exhaust gas passage components.

Patent References 6 and 7 teach ferritic steels with a Cr content of 10 to less than 15% that improve the corrosion resistance against condensed moisture needed by mufflers and other low-temperature components and also the high-temperature strength needed by exhaust manifolds and other high-temperature components. But they merely assess workability in terms of proof stress, while offering nothing specific with regard to high-temperature oxidation resistance. Patent References 6 and 7 are not directed to the goal of concurrently and consistently improving high-temperature oxidation resistance and formability with good reproducibility, and are silent regarding methods for achieving this objective. From the viewpoint of fabrication into exhaust gas passage components of various complex shapes, therefore, the steels taught by Patent References 6 and 7 cannot be considered steels that fully meet all formability requirements.

Patent Reference 1

JP-A-Hei 3(1991)-274245 (p3, upper right column, line 1 – p4, upper right column, line 9)

Patent Reference 2

JP-A-Hei 5(1993)-125491 (paragraphs 0012 – 0016)

Patent Reference 3

JP-A-Hei 7(1995)-11394 (paragraphs 0014 – 0021, 0028, 0029, Table 6, Figure 1)

Patent Reference 4

JP-A-Hei 7(1995)-145453 (paragraphs 0011 – 0021)

Patent Reference 5

JP-A-Hei 10(1998)-147848 (paragraphs 0003 – 0005, 0014)

Patent Reference 6

JP-A-Hei 10(1998)-204590 (paragraphs 0026 – 0036, 0072)

Patent Reference 7

JP-A-Hei 10(1998)-204591 (paragraphs 0028 – 0037, 0074)

As explained in the foregoing, steel sheet for automobile exhaust gas passage components is now being required to contribute to greater component design freedom by offering excellent formability that enables fabrication into complicated shapes by a diversity of forming methods. But this need should best be met while maintaining high-temperature strength and high-temperature oxidation resistance at 800 – 900 °C on a par with SUS430J1L, and also ensuring excellent low-temperature toughness. As can be seen from the aforesaid Patent References, however, no steel sheet has yet been developed that is concurrently improved to a high degree in all of formability, high-temperature strength, high-temperature oxidation resistance, and low-temperature toughness.

An object of the present invention is to provide a new ferritic heat-resistant steel that concurrently offers excellent formability enabling ready application to complexly configured automobile exhaust gas passage components, excellent high-temperature strength and high-temperature oxidation resistance enabling it to withstanding use at 900 °C and excellent low-temperature toughness having an energy transition temperature of minus 50 °C or lower, and that is lowered in cost by reducing Cr content to below 11 mass percent.

SUMMARY OF THE INVENTION

The inventors carried out a study to determine why excellent formability, high-temperature strength, high-temperature oxidation resistance, and low-temperature toughness have not yet been concurrently achieved in a steel sheet. Based on our findings, we concluded that a major cause is the fact that no means has been found for concurrently establishing with high stability and good reproducibility the properties of formability and high-temperature oxidation resistance among the foregoing properties. Then, in an ensuing in-depth study, the inventors discovered that when the austenite balance is adjusted in the manner of Equation (3) set out below, then, as shown by Equation (2) set out below, a region of Si and Cr content exists in which both excellent formability and excellent high-temperature oxidation resistance can be concurrently established.

Moreover, in evaluating workability into complexly configured exhaust gas passage components, the property of deep drawability among the different aspects of formability cannot be disregarded. It was found that an effective way to improve the deep drawability of a heat resistance ferritic steel added with Nb is to add Ti in combination with the Nb. The inventors further learned that deep drawability (average plastic strain ratio r_{AV}) and the in-plane anisotropy thereof (plastic anisotropy Δr) can be improved by partially recrystallizing the hot-rolled sheet.

It should be noted, however, that Ti addition degrades low-temperature toughness. It was found that combined addition of Cu and B more effectively improved the low-temperature toughness than did addition of Cu alone.

0018   When the amount of added Cu was progressively increased, however, an abnormal oxidation-inducing phenomenon was observed to appear abruptly. Further, an appropriate range of Cu enabling concurrent improvement of low-temperature toughness and high-temperature oxidation resistance was discovered.

The present invention was accomplished based on the foregoing findings.

Specifically, the aforesaid object is achieved by a ferritic steel sheet concurrently improved in formability, high-temperature oxidation resistance, high-temperature strength, and low-temperature toughness comprising, in mass percent, C : not more than 0.02%, Si : 0.7 – 1.1%, Mn : not more than 0.8%, Ni : not more than 0.5%, Cr : 8.0 to less than 11.0%, N : not more than 0.02%, Nb : 0.10 – 0.50%, Ti : 0.07 – 0.25%, Cu : 0.02 – 0.5%, B : 0.0005 – 0.02%, V : 0 (no addition) – 0.20%, preferably 0.01 – 0.20%, one or both of Ca and Mg : 0 (no addition) – 0.01% in total, preferably 0.0003 – 0.01% in total, one or more elements among Y and rare earth elements : 0 (no addition) – 0.20% in total, preferably 0.01 – 0.20% in total, and the balance of Fe and unavoidable impurities, and having a chemical composition satisfying all of Equations (1) – (3):

$$3\,Cr + 40\,Si \geq 61 \,\ldots\ldots\ldots\,(1)$$

$$Cr + 10\,Si \leq 21 \,\ldots\ldots\ldots\,(2)$$

$$420\,C - 11.5\,Si + 7\,Mn + 23\,Ni - 11.5\,Cr - 12\,Mo + 9\,Cu - 49\,Ti - 25\,(Nb + V) - 52\,Al + 470\,N + 189 \leq 70 \,\ldots\ldots\ldots\,(3).$$

The steel sheet may further include Mo : not more than 0.50% and Al : not more than 0.10%.

Each element symbol in Equations (1) – (3) is replaced by a value representing the content of the element in mass percent. In Equation (3), symbols of elements not contained are replaced by zero.

In the present invention, the aforesaid steel sheet may have a metallic structure obtained by cold rolling and annealing a partially recrystallized hot-rolled sheet. A "partially recrystallized hot-rolled sheet" as termed here means a hot-rolled sheet 10 – 90 vol% of whose structure is accounted for by recrystallized grains and the remainder of which is accounted for by un-recrystallized grains. The amount of recrystallized grains present can be ascertained by observing a cross-section of the hot-rolled sheet with an optical microscope. By "hot-rolled sheet" is meant the steel sheet that has been subjected to hot rolling and may have been subjected to heat treatment after hot rolling but has not be subjected to cold rolling. The final metallic structure obtained by conducting cold rolling and annealing is totally recrystallized.

In the present invention, further, the aforesaid steel sheet may have a metallic structure obtained by cold rolling and annealing a tatally recrystallized hot-rolled sheet. A "tatally recrystallized hot-rolled sheet" as termed here means a hot-rolled sheet more than 90 vol% of whose structure is accounted for by recrystallized grains.

The steel sheet provided by the present invention is particularly one used as fabricated into an automobile engine exhaust gas passage component.

BRIEF EXPLANATION OF THE DRAWINGS

FIG. 1 is a graph showing how Ti content and difference between partial and complete recrystallization after hot rolling affected r value (r_D) at 45 degrees to the rolling direction in ferritic steels whose basic composition was $10 \, \text{Cr} - 0.9 \, \text{Si} - 0.3 \, \text{Nb} - 0.1 \, \text{V} - 0.1 \, \text{Cu}$.

FIG. 2 is a graph showing how Cu content affected energy transition temperature and amount of oxidation increase after 900 °C x 200 hour heating in the atmosphere in ferritic steels whose basic composition was $10 \, \text{Cr} - 0.9 \, \text{Si} - 0.3 \, \text{Nb} - 0.1 \, \text{V} - 0.001 \, \text{B}$.

FIG. 3 is a graph showing how Cr content and Si content affected high-temperature oxidation resistance and formability in ferritic steels whose basic composition was $8 \, \text{to} 14 \, \text{Cr} - 0.5 \, \text{to} \, 1.0 \, \text{Si} - 0.3 \, \text{Nb} - 0.1 \, \text{Ti} - 0.1 \, \text{V} - 0.1 \, \text{Cu}$.

FIG. 4 is a graph showing how elongation at 45 degrees to the rolling direction in a room-temperature tensile test varied with AM value ($AM = 420 \, \text{C} - 11.5 \, \text{Si} + 7 \, \text{Mn} + 23 \, \text{Ni} - 11.5 \, \text{Cr} - 12 \, \text{Mo} + 9 \, \text{Cu} - 49 \, \text{Ti} - 25 \, (\text{Nb} + \text{V}) - 52 \, \text{Al} + 470 \, \text{N} + 189$) in ferritic steels whose basic composition was $8 \, \text{to} 14 \, \text{Cr} - 0.5 \, \text{to} \, 1.0 \, \text{Si} - 0.3 \, \text{Nb} - 0.1 \, \text{Ti} - 0.1 \, \text{V} - 0.1 \, \text{Cu}$ and that satisfied Equations (1) and (2).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 shows how Ti content and difference between partial and complete recrystallization after hot rolling affected r value (r_D) at 45 degrees to the rolling direction in ferritic steels whose basic composition was $10 \, \text{Cr} - 0.9 \, \text{Si} -$

0.3 Nb − 0.1 V − 0.1 Cu. The partially recrystallized hot-rolled sheets were 4.0 mm-thick hot-rolled sheets heat treated at 700 − 1000 °C for 1 minute to have a structure 10 − 90 vol% of which was accounted for by recrystallized grains. The totally recrystallized hot-rolled sheets were 4.0 mm-thick hot-rolled sheets heat treated at about 1050 °C for 1 minute. The hot-rolled sheets were cold rolled to 2.0 mm and totally recrystallized by annealing at 1050 °C, whereafter tensile test pieces were cut from them. As can be seen in FIG. 1, the r_D value rose sharply when Ti was added to a content of 0.07 mass% or more. Moreover, the r_D value was improved markedly over the full range of Ti content by partially recrystallizing the steel sheets after hot rolling.

While it is not altogether clear what caused these improvements, it is likely that Ti, whose carbonitride producing capability is stronger than that of Nb, fixed C and N, and since this reduced solid solution C and N, the purity of the matrix was increased to a high level that promoted development of (111) plane aggregate texture favorable for improvement of workability during recrystallization at final annealing. This effect is thought to manifest itself when the Ti content reaches 0.07 mass% or more. On the other hand, it is likely that partial recrystallization of the hot-rolled sheet uniformly produced fine Nb-Ti precipitates that suppressed development of (100) plane aggregate texture thought to be detrimental to workability improvement and promoted development of (111) plane aggregate texture.

FIG. 2 shows how Cu content affected energy transition temperature and amount of oxidation increase after 900 °C x 200 hour heating in the atmosphere in ferritic steels whose basic composition was 10 Cr − 0.9 Si − 0.3 Nb − 0.1 V − 0.001 B. The specimens used were totally recrystallized steel sheets obtained by cold rolling partially crystallized 4.0 mm-thick hot-rolled sheets to a thickness of 2.0 mm and then finally annealing them at 1050 °C. The energy transition temperature was ascertained by a Charpy impact test. No. 5 test pieces (2 mm width) were taken in accordance with JIS Z 2202 so that the impact direction would be parallel to the rolling direction, the test was conducted at minus 100 to plus 25 °C in accordance with JIS Z 2242, and the energy transition temperature was determined from the relationship between the test temperature and the absorbed energy.

Oxidation amount increase was determined in accordance with JIS Z 2281 by measuring the weight increase of the test piece when it was maintained at 900 °C in the atmosphere continuously for 200 hours. As can be seen form FIG. 2, in a ferritic steel containing an appropriate amount of B, slight addition of Cu at around 0.02 mass% effectively produced an improvement in low-temperature toughness. However, it was newly discovered that when the amount added exceeds 0.5 mass%, the oxidation resistance degenerates rapidly.

The reasons for the foregoing observations has not yet been fully ascertained, it is likely regarding low-temperature toughness that occurrence of twin crystal, a cause of low-temperature brittleness, was suppressed, while it is likely regarding occurrence of abnormal oxidation that destabilization of the matrix phase balance caused by Cr and Si oxidation was aggravated by Cu.

FIG. 3 shows how Cr content and Si content affected high-temperature oxidation resistance and formability in ferritic steels whose basic composition was 8 to14 Cr − 0.5 to 1.0 Si − 0.3 Nb − 0.1 Ti − 0.1 V − 0.1 Cu. The specimens were prepared by the process explained regarding FIG. 2. The 0.2% proof stress at 45 degrees to the rolling direction determined in a room-temperature tensile test was used as an index of formability. When this value exceeded 300 MPa, it was judged that as a material for exhaust gas passage components the steel was basically lacking in formability capable of meeting the needs of various forming methods. As can be seen from FIG. 3, low content of Cr and Si resulted in occurrence of abnormal oxidation during 900 °C x 100 hour heating in the atmosphere. On the other hand, formability deteriorated with increasing Cr and Si content. There was, however, found to be a Cr-Si combination region in which satisfactory high-temperature oxidation resistance at 900 °C and satisfactory formability can both be obtained. The existence of such a region was not known heretofore. Therefore, despite the development of various ferritic heat-resistant steels, all were inferior in either high-temperature oxidation resistance or formability and no steel emerged that could satisfy both requirements reliably and with good reproducibility.

The region in which excellent high-temperature oxidation resistance and formability can both be obtained is that in which the blank circle plots are present in FIG. 3. This region is delimited by Equations (1) and (2):

$$3\,Cr + 40\,Si \geq 61 \quad \ldots\ldots\ldots (1)$$

$$Cr + 10\,Si \leq 21 \quad \ldots\ldots\ldots (2)$$

FIG. 4 shows how elongation in a room-temperature tensile test varied with AM value (AM = 420 C − 11.5 Si + 7 Mn + 23 Ni − 11.5 Cr − 12 Mo + 9 Cu − 49 Ti − 25 (Nb + V) − 52 Al + 470 N + 189) in ferritic steels whose basic composition was 8 to14 Cr − 0.5 to 1.0 Si − 0.3 Nb − 0.1 Ti − 0.1 V − 0.1 Cu and that satisfied Equations (1) and (2). AM value represents the balance between ferrite phase and austenite phase. As can be seen from FIG. 4, high ductility was obtained only in the region of an AM value not more than 70 and degenerated precipitously when AM exceeded 70. Thus formability and high-temperature oxidation resistance are concurrently improved only when Equation (3) is satisfied in addition to Equations (1) and (2):

$$420\,C - 11.5\,Si + 7\,Mn + 23\,Ni - 11.5\,Cr - 12\,Mo + 9\,Cu - 49\,Ti -$$
$$25\,(Nb + V) - 52\,Al + 470\,N + 189 \leq 70 \quad \ldots\ldots\ldots (3).$$

Features defining the present invention will now be explained.

C and N are generally effective for improving creep strength, creep rupture strength and other high-temperature strength properties. In a ferritic steel, however, low-temperature toughness is degraded by a high content of C and N. This makes it necessary to increase the amount of added Nb and Ti in order to stabilize C and N as carbonitrides. The result is higher cost. On the other hand, an attempt to markedly lower C and N content makes steelmaking more onerous, which also increases cost. Through various studies it was found that in the present invention a content of up to 0.02 mass% is permissible for both C and N. It should be noted, however, that when the amount of added Ti and Nb is appropriately set, particularly good formability and heat resistance are obtained when the amount of (C + N) is in the range of 0.01 − 0.02 mass%. The total content of C and N combined is therefore preferably 0.01 − 0.02 mass%..

Si and Cr are both very effective for improving high-temperature oxidation property but they also harden the steel. In order to establish both excellent formability and excellent high-temperature oxidation resistance, the Si and Cr contents need to be controlled to within the range satisfying Equations (1) and (2), as explained earlier with reference to FIG. 3. In addition to being controlled based on these equations, however, upper and lower limits of Si and Cr content are further defined from the standpoint of ensuring good corrosion resistance and low-temperature toughness. To wit, the minimum required level of corrosion resistance exemplified by SUH409L cannot be achieved when the Si and Cr contents are too small, whereas the low-temperature toughness level of the SUH409L steel cannot be realized when their contents are too high. Si content is therefore defined as 0.7 – 1.1 mass%. A more preferable range of Si content is 0.8 – 1.0 mass%. Cr content is defined as 8.0 to less than 11.0%. A more preferable range of Cr content is 9.0 to less than 11.0% and a still more preferable range of Cr content is 9.0 to less than 10.0%.

Mn hardens the steel and degrades its low-temperature toughness and formability when added in excess. Particularly in the composition system of the present invention, excessive addition of Mn is liable to adversely affect high-temperature oxidation resistance by causing generation of austenitic phase during hot use. The upper limit of Mn content is therefore defined as 0.8 mass%. In the composition system of the present invention, particularly when excellent scale adherence at the 900 °C level is required, Mn is preferably added to within the content range of 0.2 – 0.8 mass%.

Ni is effective for improving low-temperature toughness but hardens the steel and degrades its formability when added in excess. Moreover, in the composition system of the present invention, excessive addition of Ni is, like excessive addition of Mn, liable to degrade high-temperature oxidation resistance by causing generation of austenitic phase during hot use. The upper limit of Ni content is therefore defined as 0.5 mass%.

Nb is very effective for improving high-temperature strength. Since Ti is added in the present invention, substantially no Nb is fixed to C and N, so that essentially all added Nb can be considered to work effectively toward enhancing

high-temperature strength. This effect manifests itself at a content of not less than 0.10 mass%. On the other hand, excessive Nb addition degrades formability and low-temperature toughness. The Nb content is therefore defined as 0.10 – 0.50 mass%. In order to obtain still higher formability and high-temperature strength, a Nb content in the range of 0.10 – 0.40 mass% is preferable.

Ti fixes C and N and is generally known to improve grain boundary corrosion resistance. In this invention, however, it is a very important element for improving formability (particularly deep drawability). The formability improving effect of Ti appears conspicuously at content of not less than 0.07 mass% (see FIG. 1). However, excessive Ti addition degrades toughness and adversely affects product surface properties. Ti content is therefore defined as 0.07 – 0.25 mass%. For obtaining a high level of high-temperature strength, Ti is preferably added to satisfy Ti ≥ 6 (C + N). In order to obtain a product with surface properties as good as or better than SUH409L, Ti is preferably added to a content of not more than 0.20 mass%.

Mo is effective for increasing high-temperature strength but makes the steel brittle when present at a high content. In addition, Mo is very expensive. While adequate heat resistance can be secured without Mo addition by optimizing the contents of other constituent elements, Mo addition is advantageous in that it increases the freedom of composition design. When Mo is incorporated, its content is preferably not more than 0.50 mass%. When heat resistance is a bigger concern than cost, Mo can be added in excess of 0.5 mass% but should not be added in excess of 3.0 mass%, the level beyond which an extreme decline in low-temperature toughness occurs.

Cu improves low-temperature toughness. In order to markedly improve low-temperature toughness to the level required in exhaust gas passage components, however, it is important to incorporate not less than 0.02 mass% of Cu in combination with B (discussed later). When the Cu content exceeds 0.5 mass%, however, high-temperature oxidation resistance degenerates sharply (see FIG. 2). Cu content is therefore defined as 0.02 – 0.5 mass% in the present invention.

V, like Nb and Ti, is a carbonitride-forming element that is effective for improving grain boundary corrosion resistance and the toughness of sites affected by welding heat. Moreover, like Nb, V contributes to high-temperature strength improvement in the solid solution state. This effect is particularly pronounced when V is present together with Nb. In addition, V is thought to be effective for improving high-temperature oxidation resistance. However, a V content in excess of 0.20 mass% degrades workability and low-temperature toughness. When V is added, therefore, its content must be kept to not more than 0.20 mass%. For thoroughly obtaining the foregoing effects of V, it is preferably added in the range of 0.01 – 0.20 mass%.

Al is highly effective for improving high-temperature oxidation resistance. However, the composition according to the present invention is designed to enable excellent high-temperature oxidation resistance even without incorporation of Al. Excessive Al addition degrades formability, weldability and low-temperature toughness. Moreover, deoxidation by Al is not particularly necessary because the present invention calls for addition of Ti and Si. When Al is incorporated, it must be added at no more than 0.10 mass%. When adding Al in a case where formability, weldability and low-temperature toughness are particularly important, the Al content is preferably restricted to not more than 0.07 mass%.

B suppresses low-temperature brittleness and secondary work brittleness in a ferritic steel also containing Nb and Ti. This effect was found to be pronounced when B is added in combination with Cu. In order to thoroughly improve low-temperature toughness, B needs to be added at not less than 0.0005 mass%. On the other hand, excessive B addition beyond 0.02 mass% leads to generation of borides that degrade formability and degrade rather than improve low-temperature toughness. In the present invention, B is incorporated at 0.0005 – 0.02 mass% together with Cu at 0.02 – 0.5 mass%.

Ca and Mg have strong binding force with S and therefore reduce the amount of MnS generation to improve corrosion resistance. In addition, Ca and Mg are elements that in themselves effectively work to improve high-temperature oxidation resistance. When importance is attached to corrosion resistance and

high-temperature oxidation resistance, therefore, these elements can be added as required. However, addition in large amounts increases inclusions that degrade low-temperature toughness and formability. When one or both of Ca and Mg are added, therefore, the combined content thereof needs to be held to not more than

5   0.01 mass%. In order to bring out the effect of Ca and Mg addition strongly, the total of the Ca and Mg contents should preferably made 0.003 – 0.01 mass%.

Y and REMs (rare earth elements) such as La and Ce stabilize the chromium oxide coating that forms on the steel surface and, by enhancing the adherence between the steel matrix and the oxide coating, manifestly improve the

10 high-temperature oxidation resistance of the steel sheet. When high-temperature oxidation resistance is a major concern, therefore, these elements can be added as required. However, addition in large amounts not only degrades formability and low-temperature toughness but also promotes generation of inclusions that may become starting points of abnormal oxidation, meaning that high-temperature

15 oxidation resistance is degraded rather than improved. Therefore, when one or more elements selected from among Y and rare earth elements are added, the combined amount thereof must be made not more than 0.20 mass%. For maximizing the effect of Y and REM addition, one or more elements selected from among these elements ·should preferably be added to a combined total of 0.01 – 0.20 mass%.

20 As additional elements, one or more of Zr, Hf, Ta, W, Re and Co can be included for their ability to improve high-temperature strength. Since excessive addition of these elements hardens the steel, however, they must, when incorporated, be added to a combined content of not more than 3.0 mass%. The preferable amount is not more than 0.5 mass% in total.

25 The content of P, S, O, Zn, Sn, Pb and other common impurity elements is preferably reduced to the lowest level possible in order to ensure good formability and low-temperature toughness. Specifically, these elements should, at the most lenient, be restricted to P : not more than 0.04 mass%, S : not more than 0.03 mass%, O : not more than 0.02 mass%, Zn : not more than 0.10 mass%, Sn :

30 not more than 0.10 mass%, and Pb : not more than 0.10 mass%. At the actual

production site, more severe restrictions can be imposed in accordance with the product quality desired.

As explained earlier, Equations (1) – (3) define the composition range required for concurrent improvement of formability and high-temperature oxidation resistance. Although no particular lower limit is specified for the value (AM value) of the left side of Eqution (3), a steel with a low AM value ordinarily contains liberal amounts of ferrite generating elements like Si, Cr, Mo, Ti, Nb, V and Al. When large amounts of these elements are contained, formability and low-temperature toughness degenerate. Studies showed that it is preferable to regulate the constituents so that the AM value is 40 or higher.

Satisfying the aforesaid chemical composition concurrently improves formability, high-temperature oxidation resistance, high-temperature strength and low-temperature toughness.

In order to further improve the formability realized in this way, it is highly effective to subject the hot-rolled sheet to partial recrystallization treatment followed by cold rolling and annealing. Specifically, the r value, an index of deep drawability, can be markedly improved by the steps of making a hot-rolled sheet 10 – 90 vol% of whose structure is accounted for by recrystallized grains and the remainder of which is accounted for by un-recrystallized grains, cold rolling the hot-rolled sheet, and totally recrystallizing it by annealing (see FIG. 1). The steel sheet having the metallic structure obtained in this manner possesses formability fully capable of responding to the increasingly severe shape requirements of today's exhaust gas passage components.

Partial recrystallization of the hot-rolled sheet can be carried out directly during hot rolling process or by heating conducted between hot rolling and cold rolling.

Partial recrystallization during hot rolling can, for instance, be conducted by hot rolling in the temperature range of 950 - 1250 °C, coiling, and cooling in the coiled state. Optimum conditions can be selected in accordance with the facility specifications and the hot-rolling pass schedule. Partial recrystallization by heating after hot rolling can be conducted, for example, by heating the steel sheet

cooled after hot rolling in the temperature range of 850 - 1000 °C. The heating can be carried out at any stage before cold rolling.

The hot-rolled sheet partially recrystallized by one of the foregoing methods is then totally recrystallized by annealing. The cold rolling is conducted at a

5   reduction in the range of, for example, 30 – 90%. When the steel sheet is to be used in an automobile exhaust gas passage component, the final sheet thickness is adjusted to, for example, about 0.4 – 1.2 mm. The annealing temperature is preferably in the range of, for instance, 950 - 1150 °C. The ferritic steel sheet obtained is excellent in formability and low-temperature toughness and these

10 properties are retained even after fabrication into welded steel tube.

In case an article having been formed should have a beautiful surface appearance and make much of good looking outer surface, it is preferable to use the totally recrystallized hot-rolled sheet to form the article. The totally recrystallized hot-rolled sheet can be obtained by subjecting the hot-rolled sheet into a heat

15 treatment at the temperatures between 950 and 1100 °C

Example 1

Ferritic steels having the chemical compositions shown in Tables 1 and 2 were made using a high-frequency vacuum melting furnace and cast into

20 30-Kg ingots. The ingots were hot-forged and then hot-rolled into 4.0 mm hot-rolled sheets. The hot rolling was conducted at a hot-rolling temperature of 700 - 1250 °C and a draft (rolling reduction) per pass of about 30%. Each hot-rolled sheet was water cooled and then held at 900 - 1000 °C for 1 minute. The cross-sectional metallic structure of the hot-rolled sheet was observed with an optical microscope.

25 Recrystallized grains were found to account for 10 – 90 vol.% of every specimen, the balance being un-recrystallized structure. It was thus ascertained that partial recrystallization had been achieved. The partially recrystallized hot-rolled sheets were cold rolled to a thickness of 2 mm and thereafter totally recrystallized by annealing for 1 minute at 1050 °C to afford cold-rolled annealed sheets. Nos. 1 –

30 21 in Table 1 are ferritic steels satisfying the chemical composition defined by the present invention. Nos. 22 – 31 in Table 2 are comparative steels not meeting

compositional requirements of the present invention. Among the comparative steels, No. 22 corresponds to SUH409L and No. 23 to SUS430J1L.

Table 1

(Mass%)

No.	C	Si	Mn	Ni	Cr	Mo	Cu	Ti	Nb	V	Al	B	N	Other	3Cr+40Si	Cr+10Si	AM value
1	0.002	0.93	0.04	0.02	8.06	tr.	0.02	0.14	0.31	0.03	0.08	0.0005	0.003	—	61.4	17.4	69.3
2	0.009	0.78	0.78	0.09	10.11	0.01	0.10	0.09	0.33	0.05	0.06	0.0010	0.008	—	61.5	17.9	62.6
3	0.010	1.00	0.20	0.11	9.52	tr.	0.05	0.20	0.20	0.20	0.01	0.0050	0.009	—	68.6	19.5	60.5
4	0.009	0.79	0.78	0.10	10.45	0.05	0.12	0.14	0.29	0.15	0.01	0.0037	0.007	—	63.0	18.4	56.7
5	0.009	0.88	0.77	0.10	9.60	tr.	0.11	0.14	0.28	0.04	tr.	0.0026	0.007	—	64.0	18.4	69.4
6	0.010	0.71	0.08	0.10	10.99	tr.	0.10	0.14	0.34	0.06	0.01	0.0011	0.007	—	61.4	18.1	48.3
7	0.009	0.80	0.18	0.10	10.27	0.14	0.10	0.14	0.32	0.03	0.03	0.0030	0.007	—	62.8	18.3	54.4
8	0.009	0.80	0.18	0.10	10.40	tr.	0.48	0.15	0.33	0.07	0.02	0.0023	0.007	—	63.2	18.4	56.8
9	0.011	0.80	0.18	0.10	10.81	0.46	0.11	0.15	0.33	0.05	tr.	0.0012	0.006	—	64.4	18.8	45.1
10	0.006	0.91	0.22	0.02	10.46	0.03	0.21	0.24	0.25	0.04	0.01	0.0023	0.007	—	67.8	19.6	48.1
11	0.005	0.92	0.31	0.12	10.49	0.01	0.15	0.12	0.49	0.04	0.01	0.0017	0.008	—	68.3	19.7	50.2
12	0.012	0.85	0.44	0.11	10.52	0.01	0.12	0.13	0.11	0.19	0.01	0.0020	0.009	—	65.6	19.0	59.7
13	0.014	0.89	0.21	0.47	10.36	tr.	0.06	0.11	0.25	0.06	0.01	0.0091	0.009	—	66.7	19.3	68.9
14	0.018	0.95	0.22	0.10	10.38	tr.	0.06	0.09	0.38	0.05	0.01	0.0014	0.003	—	69.1	19.9	56.4
15	0.002	1.01	0.26	0.10	10.54	0.42	0.10	0.15	0.39	0.03	0.01	0.0016	0.020	—	72.0	20.6	48.3
16	0.004	1.09	0.19	0.12	10.10	0.10	0.11	0.15	0.28	0.03	0.02	0.0011	0.009	—	73.9	21.0	54.0
17	0.005	0.98	0.15	0.10	9.88	0.11	0.10	0.14	0.29	0.03	tr.	0.0021	0.008	Ca:0.004	68.8	19.7	58.0
18	0.008	0.77	0.12	0.10	10.09	tr.	0.09	0.14	0.29	0.02	tr.	0.0037	0.007	Mg:0.001	61.1	17.8	60.1
19	0.003	0.88	0.04	0.11	8.61	tr.	0.05	0.19	0.33	0.01	tr.	0.0019	0.007	La:0.01 Ce:0.04	61.0	17.4	69.9
20	0.007	0.71	0.10	0.11	10.87	tr.	0.10	0.11	0.25	0.02	tr.	0.0015	0.008	Y:0.03	61.0	18.0	54.5
21	0.003	0.75	0.61	0.12	10.25	tr.	0.11	0.09	0.20	tr.	tr.	0.0005	0.002	—	60.8	17.8	63.3

tr. : Trace

Table 2

(Mass%)

No.	C	Si	Mn	Ni	Cr	Mo	Cu	Ti	Nb	V	Al	B	N	Other	3Cr+40Si	Cr+10Si	AM value
22	0.010	0.51*	0.15	0.11	10.92	tr.	tr.*	0.24	tr.*	tr.	0.08	tr.*	0.008	–	53.2*	16.0	53.2
23	0.009	0.56*	0.16	0.37	18.74*	tr.	0.43	tr.*	0.41	0.07	0.01	tr.*	0.014	–	78.6	24.3*	-21.6
24	0.009	0.96	1.07*	0.14	13.58*	tr.	0.10	tr.*	0.51	0.04	0.02	tr.*	0.009	–	79.1	23.2*	26.6
25	0.023*	0.56*	0.80	0.10	11.71*	tr.	0.24	0.11	0.59*	0.03	0.01	0.0009	0.004	–	57.5*	17.3	48.1
26	0.010	0.68*	0.17	0.09	8.73	tr.	0.10	0.10	0.31	0.01	tr.	0.0022	0.009	–	53.4*	15.5	80.5*
27	0.007	0.92	0.21	0.10	10.42	0.06	0.61*	0.14	0.26	0.03	0.01	0.0014	0.008	–	68.1	19.6	59.2
28	0.008	0.90	0.15	0.10	10.39	0.01	0.10	0.35*	0.24	0.02	tr.	0.0017	0.008	–	67.2	19.4	46.8
29	0.006	1.24*	0.16	0.01	8.39	0.02	0.11	0.17	0.29	0.02	0.01	0.0021	0.008	–	74.8	20.8	70.0
30	0.009	0.88	0.23	0.11	10.23	tr.	0.13	0.13	0.31	0.04	0.21*	tr.*	0.007	La:0.01 Ce:0.04	65.9	19.0	47.6
31	0.010	0.96	0.25	0.09	9.96	tr.	0.09	0.16	0.30	0.03	0.01	0.0152*	0.007	Mg:0.001	68.3	19.6	58.9

tr. : Trace   * : Outside invention range

A test piece cut from each cold-rolled annealed sheet was subjected to a tensile test, a Charpy impact test, a high-temperature tensile test, and a high-temperature oxidation test.

Formability was evaluated based on the 0.2% strength, breaking
5   extension and plastic strain ratio determined by the tensile test. No. 13B test pieces (prescribed by JIS Z 2201) cut from each steel sheet specimen in directions parallel, 45 degrees and 90 degrees to the rolling direction were used as the tensile test pieces. 0.2% strength and breaking extension were determined by subjecting the test piece taken 45 degrees with respect to the rolling direction to the tests prescribed by
10 JIS Z 2241. Plastic strain ratio was determined in accordance with JIS Z 2254 using the test pieces taken in all three of the aforesaid directions. More specifically, the plastic strain ratio in each direction was calculated from the ratio between the lateral strain and thickness direction strain under application of a 15% uniaxial tensile pre-strain, and the average plastic strain ratio r_{AV} and in-plane plastic anisotropy
15 Δr were determined in accordance with the following equations:

$$r_{AV} = (r_L + 2r_D + r_T) / 4$$
$$\Delta r = (r_L - 2r_D + r_T) / 2$$

where

r_L = Plastic strain ratio parallel to rolling direction
20 r_D = Plastic strain ratio 45 degrees to rolling direction

r_T = Plastic strain ratio 90 degrees to rolling direction.

The Charpy impact test was conducted by the method explained with reference to FIG. 2. The energy transition temperature was determined and used as an index of low-temperature toughness.

25 The high-temperature tensile test was conducted in accordance with JIS G 0657 using the tensile test piece taken at 45 degrees. The 0.2% strength at 900 °C was determined and used as an index of high-temperature strength.

The high-temperature oxidation test was conducted in accordance
30 with JIS Z 2281 by determining the amount of oxidation increase after heating at 900 °C for 200 hours in the atmosphere. The result was used as an index of high-temperature oxidation resistance.

The results of the foregoing tests are shown in Table 3.

Table 3

	No.	Room-temp. 0.2% proof stress (Mpa)	Elongation at room tem. in tensile test (%)	Ave. plastic strain ratio r_{AV}	In-plane plastic anisotropy Δr	Energy transition temp. (°C)	High-temp. 0.2% proof stress[1] (Mpa)	Weight gain after Oxidation test[2] (mg/cm^2)
Invention Examples	1	275	37	1.7	0.3	−50	14	1.2
	2	280	36	1.6	0.4	−75	15	1.2
	3	295	33	1.3	0.2	−50	13	1.1
	4	285	35	1.4	0.2	−50	13	1.2
	5	280	35	1.4	0.3	−50	13	1.2
	6	280	36	1.4	0.3	−75	15	1.3
	7	285	35	1.3	0.3	−50	14	1.1
	8	285	35	1.4	0.2	−50	14	1.0
	9	295	34	1.3	0.2	−50	14	1.1
	10	295	33	1.3	0.3	−50	13	0.9
	11	290	34	1.4	0.3	−50	16	1.0
	12	290	34	1.3	0.4	−50	12	1.0
	13	295	33	1.3	0.4	−50	13	1.1
	14	295	33	1.3	0.3	−50	14	0.9
	15	300	33	1.3	0.4	−50	14	0.7
	16	300	33	1.3	0.3	−50	13	0.8
	17	295	33	1.3	0.3	−50	13	0.6
	18	280	35	1.5	0.3	−50	13	0.6
	19	280	35	1.4	0.2	−50	13	0.4
	20	280	36	1.6	0.5	−50	12	0.3
	21	280	35	1.3	0.5	−50	11	1.4
Comparative Examples	22	265	33	1.1*	0.7*	−75	9*	18.0*
	23	335*	32*	1.0*	0.7*	−50	12	0.8
	24	355*	31*	1.1*	0.7*	−25*	13	1.0
	25	300	35	0.9*	0.5	−25*	15	5.0*
	26	410*	29*	1.3	0.0	−50	13	9.0*
	27	295	33	1.3	0.4	−25*	12	11.0*
	28	290	33	1.3	0.5	−25*	12	1.3
	29	300	33	1.3	0.4	−25*	12	1.2
	30	290	33	1.3	0.5	−25*	13	0.5
	31	295	33	1.3	0.5	−25*	13	0.7

* : Object of invention not achieved   1) 900 °C   2) 900 °C x 200hr

As can be seen from Table 3, the steels Nos. 1 – 21, examples of the present invention, all had softness (0.2% proof stress) falling about midway between SUH409L (No. 22) and SUS430J1L (No. 23) and ductility (elongation) similar to SUH409L. They were superior to SUH409L and SUS430J1L in deep drawability,

5   i.e., in average plastic strain ratio r_{AV} and in-plane plastic anisotropy Δr. Their low-temperature toughness (energy transition temperature) performance was also excellent, matching that of SUH409L. The invention steels were clearly superior to SUH409L and substantially matched the performance of SUS430J1L in 900 °C heat resistance (high-temperature strength and high-temperature oxidation

10   resistance). In short, the steels of the present invention achieved excellent formability while also thoroughly maintaining high-temperature strength, high-temperature oxidation resistance and low-temperature toughness.

In contrast, steel No. 22, a comparative example steel equivalent to SUH409L, was inferior in heat resistance, and No. 23, equivalent to SUS430J1L,

15   was hard and insufficient in formability. Steels Nos. 24 and 25 are types that have actually been used in automobile engine exhaust gas passage components. However, No. 24 was inferior in formability and low-temperature toughness owing to the fact that, inter alia, it was not added with Ti and had Si and Cr contents falling outside the ranges of the present invention, while No. 25 was poor in formability,

20   low-temperature toughness and high-temperature oxidation resistance because it was high in C and Nb and had Si and Cr contents falling outside the ranges of the present invention. Steel No. 26 was inferior in formability and high-temperature oxidation resistance because its phase stability was on the austenitic side. Steels No. 27 – 31 exhibited deficient low-temperature toughness because they contained elements

25   harmful to low-temperature toughness in amounts exceeding the ranges specified by the present invention.

Example 2

The steels shown in Tables 1 and 2 as from No.1 to No.10 and from

30   No.22 to 26 were hot-rolled and then subjected to the heat treatment at temperatures between 950 and 1100 °C for 1 minute, thereby to obtain the hot rolled sheet having totally recrystallized structure. The sheets obtained were cold rolled into 2.0 mm and

thereafter totally recrystallized by annealed at 1050 °C for 1 minute to afford cold rolled annealed sheets.

As same as Example 1, a piece cut from each cold-rolled annealed sheet was subjected to the test to evaluate 0.2% strength, breaking extension, plastic strain ratio and in-plane anisotropy. Further, in order to evaluate a surface appearance after formed, a piece cut from each cold-rolled annealed sheet was imposed 20 % of plastic strain in direction parallel to the rolling direction and subjected to the test to evaluate the surface roughness of the test piece surface in direction perpendicular to the rolling direction by using a contact-type surface roughness meter, the surface roughness being 10 points average roughness Rz in accordance with JIS B 0660. For comparative, the surface roughness was tested as same above for the test pieces shown in Table 3 which were derived from the partially recrystallized hot-rolled sheets and the results was shown in Table 4 as Comparative value of surface roughness.

Table 4

	No.	Room-temp. 0.2% proof stress (Mpa)	Elongation at room-temp. in tensile test (%)	Ave. plastic strain ratio r_{AV}	In-plane plastic anisotropy Δr	Surface loughness (μ m)	Comparative vale of surface roughness [1] (μ m)
Invention Examples	1	270	37	1.6	0.5	15	35
	2	275	37	1.5	0.6	20	40
	3	290	34	1.3	0.4	15	35
	4	285	35	1.4	0.4	10	30
	5	280	36	1.3	0.5	10	30
	6	275	36	1.3	0.5	15	40
	7	280	36	1.3	0.5	25	45
	8	285	35	1.4	0.6	20	40
	9	295	35	1.2	0.4	15	35
	10	290	34	1.2	0.5	15	35
Comparative Examples	22	260	34	1.0*	0.8*	30	50
	23	330	33	1.0*	0.9*	30	45
	24	350*	32*	1.0*	0.8*	25	40
	25	290	35	0.9*	0.8*	25	45
	26	420*	28*	1.2	0.4	25	40

* : Object of invention not achieved

1) Test results for the pieces of partially recrystallized hot-rolled sheets shown
   in Table 3.

In comparison with the invention examples between Table 4 and Table 3, it is seen that the test pieces derived from totally recrystallized hot-rolled sheets, those of Table 4, tend to have same or lower average plastic strain ratio and have slightly increased in-plane anisotropy than those of Table 3 for partially recrystallized hot rolled sheets. This seems to be based on the slight lowering of r value in direction 45 degree to the rolling direction in the case of totally recrystallized hot-rolled sheets. On the other hand, it is apparent that the surface roughness after formed is remarkably decreased when the totally recrystallized hot-rolled sheets are used. This means that by adoption of a treatment for totally recrystallization in the hot-rolled sheet, there is provided a steel sheet suitable for use in the article formed which requires superior fine surface appearance. Comparative examples in Table 4 are basically below in formability compared with invention examples.

Thus the present invention enables concurrent improvement of formability, high-temperature strength, high-temperature oxidation resistance and low-temperature toughness in a ferritic heat-resistant steel sheet. The ferritic steel sheet of the present invention is particularly notable in that it offers excellent formability, specifically deep drawability and isotropy thereof, capable of responding to the needs of a diversity of forming methods. In this aspect, the steel sheet of the present invention is endowed with new capabilities not envisioned by conventional ferritic heat-resistant steel sheets. It also offers high-temperature strength, high-temperature oxidation resistance and low-temperature toughness that achieve a performance level equal to or better than the steel sheets currently used in exhaust gas passage components. While conventional ferritic steel sheets have been incapable of concurrently achieving high levels of formability, high-temperature strength, high-temperature oxidation resistance and low-temperature toughness, the present invention concurrently achieves excellent performance on all of these points at a Cr content of not more than 11%. As such, the present invention enables application of ferritic heat-resistant steel to complicatedly shaped exhaust gas passage components, helps to expand the degree of freedom in designing such components, and makes a marked contribution to cost reduction.